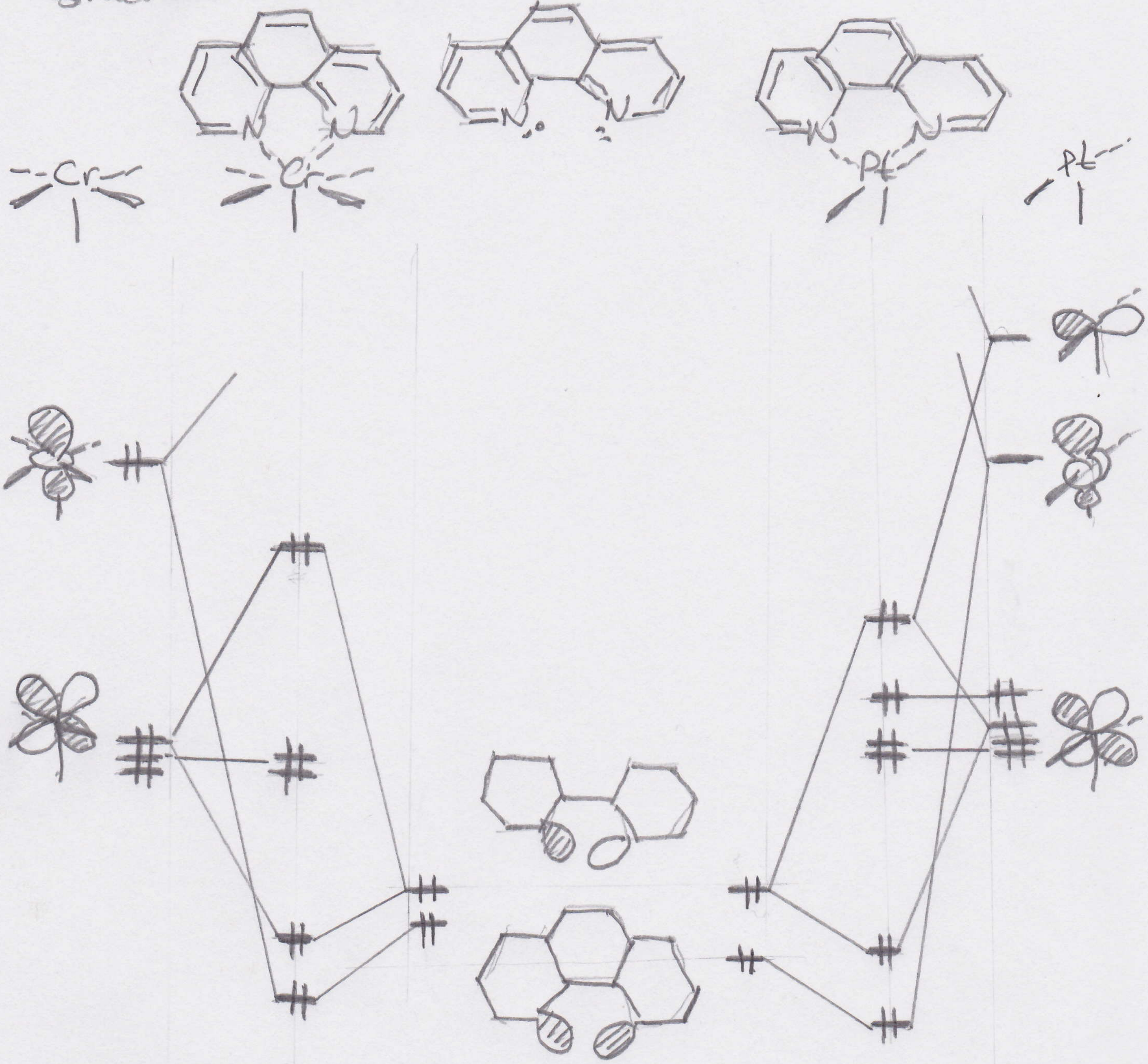
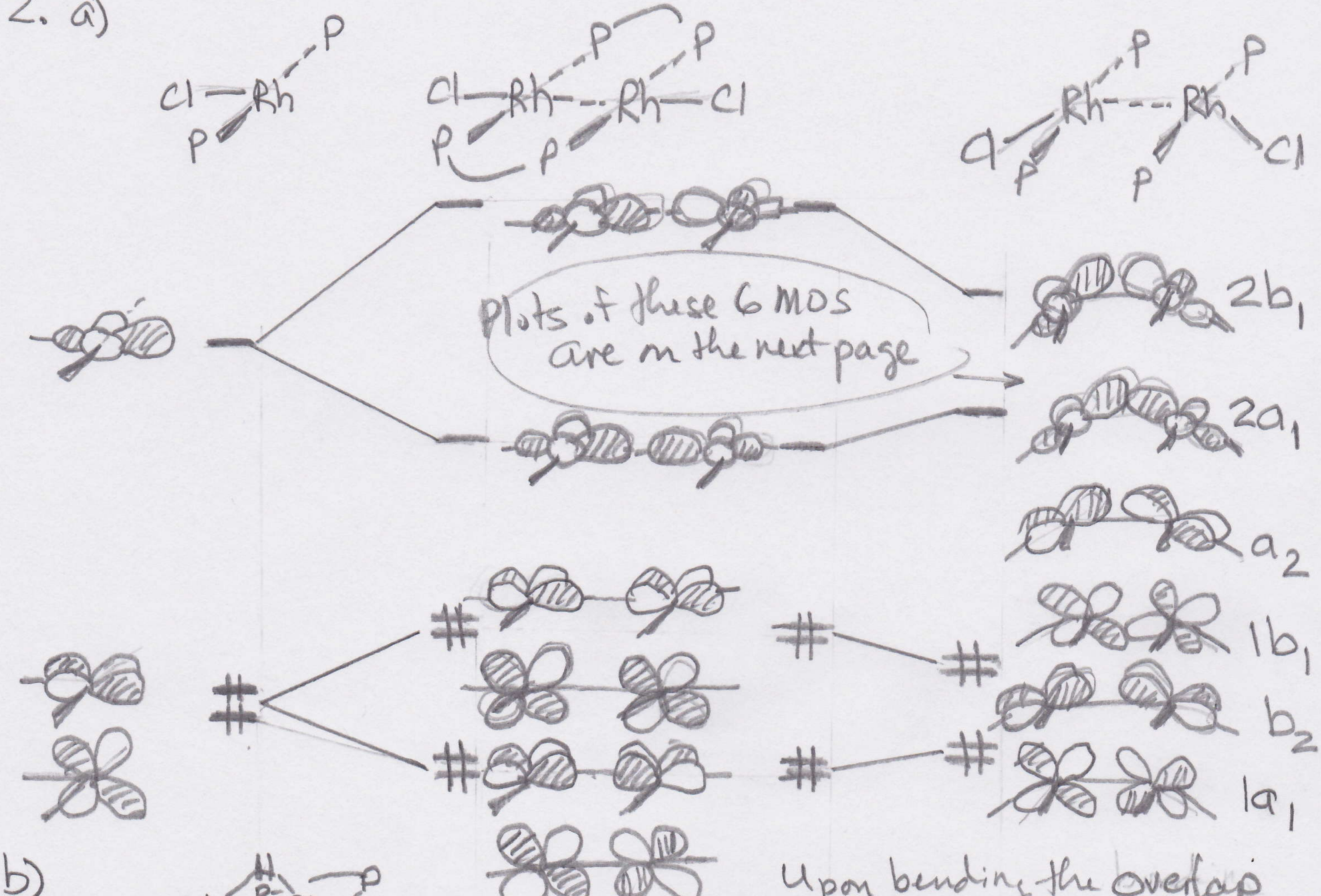
Answers – Chapter 18

1. The ground state for the $Cr(CO)_5$ and $Pt(PEt_3)_2Cl^+$ are the standard 18 and 16 electron octahedral and square planar complexes. At the transition state the metal is partially coordinated to the two nitrogens. The electronic structure can be constructed as:



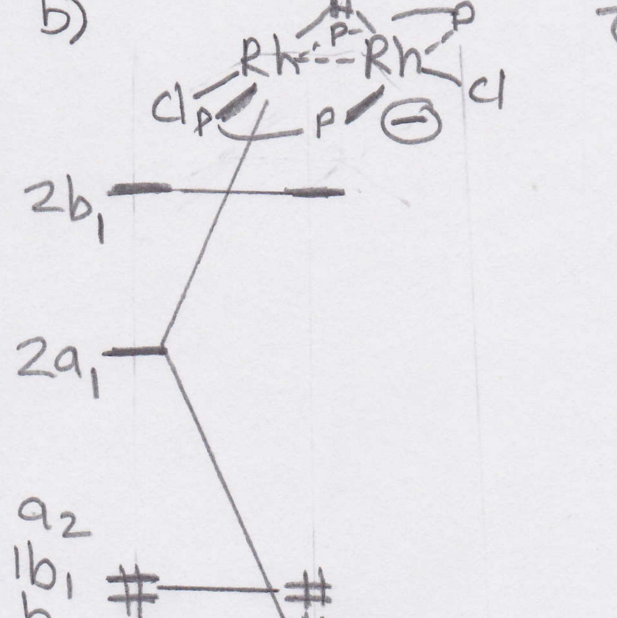
2. a)



Plots of these 6 MOS are on the next page

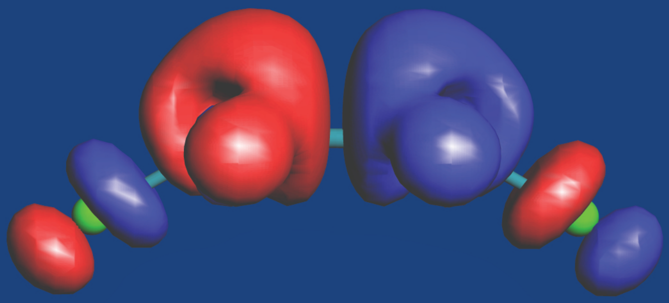
Upon bending the overlap between ML_3 units decreases so bonding goes up and antibonding goes down in energy

b)

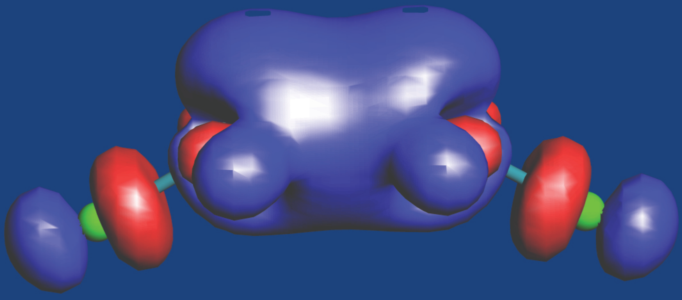


remember there are 4 more MO's with 8 electrons here

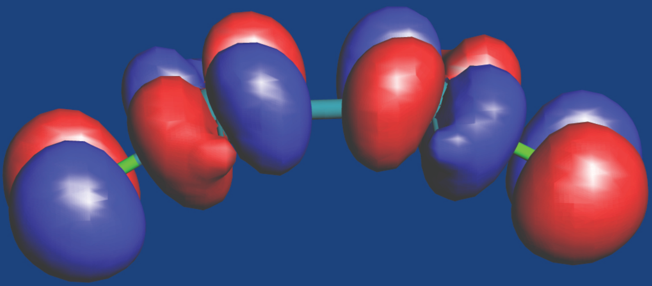
One could count 2e⁻ in the 2 Rh-H bonds - so one has Rh(1+) - a typical d^8 square planar complex. But, there is also Rh--Rh bonding in the two filled a_1 MO's. So while there is not a full Rh-Rh single bond, there must be some fractional bond order



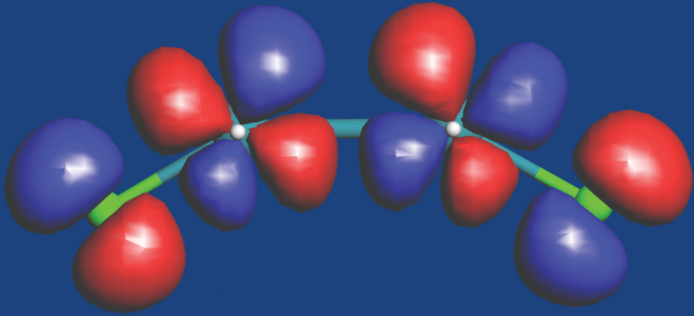
$2b_1$



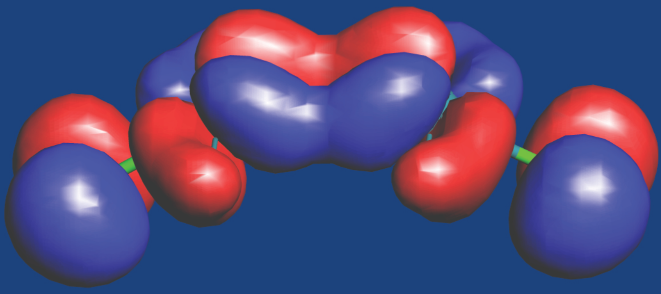
$2a_1$



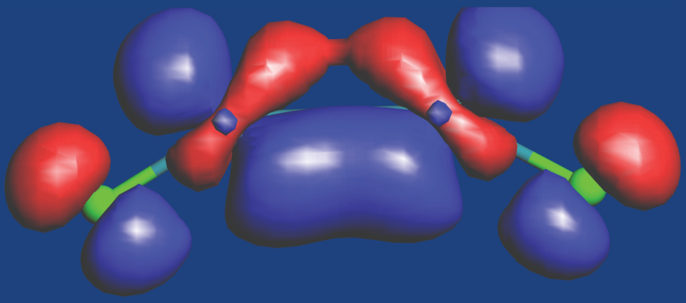
a_2



$1b_1$

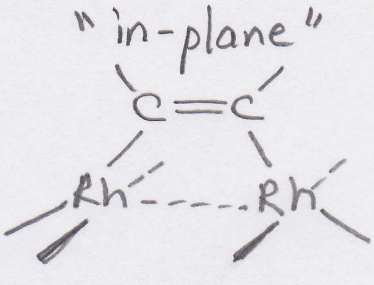


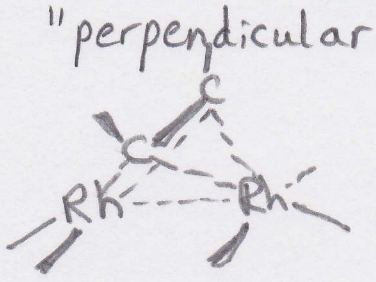
b_2

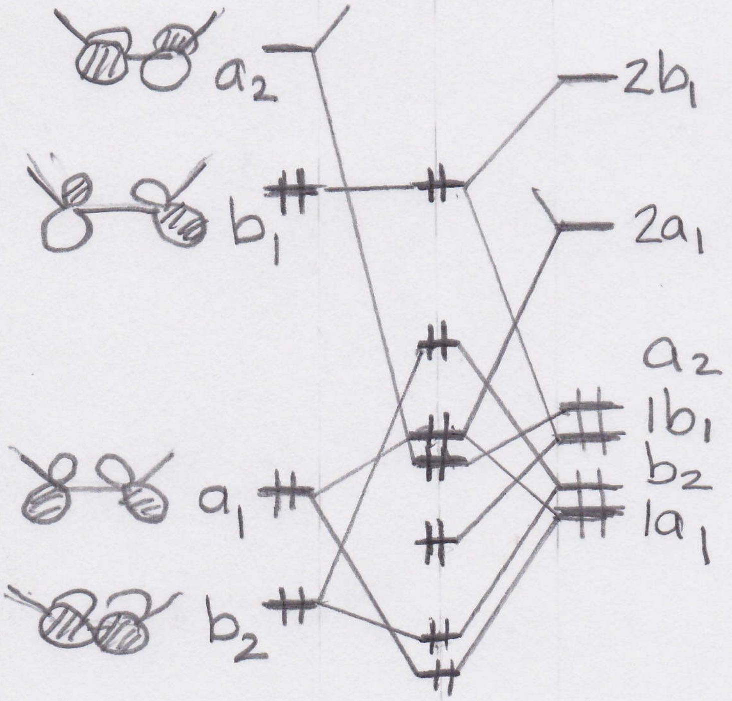


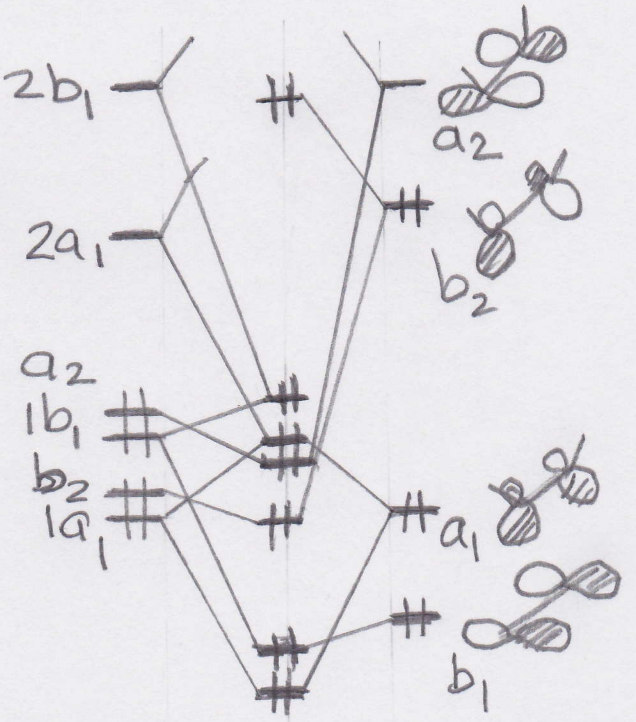
$1a_1$

c)



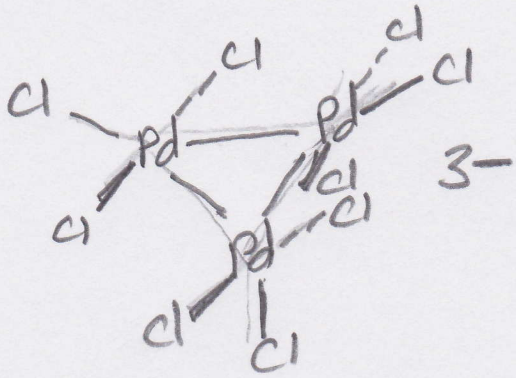


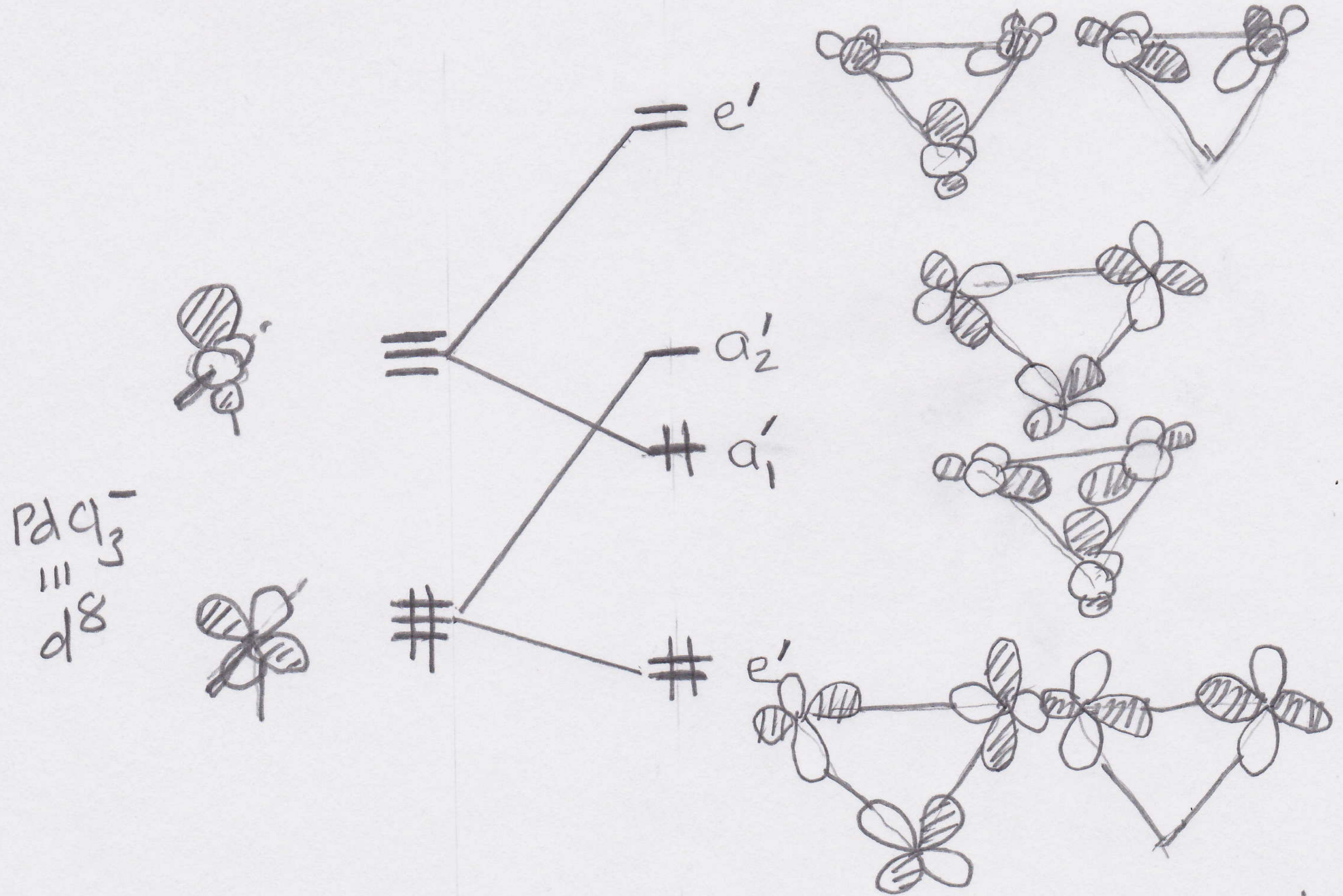




This looks complicated! But every interaction is a 2-orbital one except for 2 3-orbital combinations. Using the fragments above, the overlap in the two geometries for the a_1 and a_2 combinations are about the same, so the orbital energies in the two geometries is approximately the same, The b_1 & b_2 acetylene combinations interchange symmetries. At the in-plane geometry π^* is b_1 so the HOMO is the the "non-bonding" member of a 3 orbital interaction. On the other hand, π^* is b_2 at the perpendicular geometry and so it is the antibonding combination of a 2 orbital interaction. The HOMO is lower at the in-plane geometry. It should be more stable. (and it is!)

3.





The resultant 6 MOs have the same symmetry properties as the Walsh set in cyclopropane with the same orbital occupation. But this is not a stable structure - notice that there is something funny about the electron count.